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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Melbourne
Grattan Street
Parkville, VIC 3010
Australia

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Over the last decade, shape controlled synthesis of nanoparticles (NPs) has opened up the possibility to study heterogeneous catalysis on a variety of well-defined nanoscale crystal facets. This investigation examined using single particle surface plasmon spectroscopy (SPS) as a tool for real-time monitoring of catalytic processes and chemical intermediates during surface redox reactions (e.g., hydrogen spillover). The ultimate goal of this research is to be able to identify which crystal facets determine overall catalytic nanoparticle efficiency in heterogeneous reactions. Dark field spectroscopy was used to monitor hydrogen dissociation on single gold nanoparticles embedded in metal oxide supports. Individual gold nanorods were monitored in real-time to reveal peak position, full width at half maximum and relative intensity of the surface plasmon resonances during repeated N_2-H_2-N_2 and air-H_2-air cycles. It was found that hydrogen does not dissociate on gold nanorods at room temperature when in contact with silica and that electrons or hydrogen atoms migrate from Pt nanoparticles to Au nanoparticles through the supporting metal oxide at room temperature. The results show that hydrogen spillover, surface dissociation of reactants and surface migration of chemical intermediates can be detected and monitored in real time at the single particle level. The ultimate sensitivity of the SPS technique was determined using chemically synthesized gold nanorods as individual optical elements in a quasi-solid-state ion-gel capacitor. The smallest detectable changes occurred from 10mV applied voltages, which yielded less than 100 electrons per nanorod. An increase in electron density was found to lead to an overall increase in scattering intensity and was described for the first time using Drude model derivations. The approach involved building large nanoparticle combinatorial libraries for high throughput screening.

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Over the last decade, shape controlled synthesis of nanoparticles (NPs) has opened up the possibility to study heterogeneous catalysis on a variety of well-defined nanoscale crystal facets. This investigation examined using single particle surface plasmon spectroscopy (SPS) as a tool for real-time monitoring of catalytic processes and chemical intermediates during surface redox reactions (e.g., hydrogen spillover). The ultimate goal of this research is to be able to identify which crystal facets determine overall catalytic nanoparticle efficiency in heterogeneous reactions. Dark field spectroscopy was used to monitor hydrogen dissociation on single gold nanoparticles embedded in metal oxide supports. Individual gold nanorods were monitored in realtime to reveal peak position, full width at half maximum and relative intensity of the surface plasmon resonances during repeated N2-H2-N2 and air-H2-air cycles. It was found that hydrogen does not dissociate on gold nanorods at room temperature when in contact with silica and that electrons or hydrogen atoms migrate from Pt nanoparticles to Au nanoparticles through the supporting metal oxide at room temperature. The results show that hydrogen spillover, surface dissociation of reactants and surface migration of chemical intermediates can be detected and monitored in real time at the single particle level. The ultimate sensitivity of the SPS technique was determined using chemically synthesized gold nanorods as individual optical elements in a quasi-solid-state ion-gel capacitor. The smallest detectable changes occurred from 10mV applied voltages, which yielded less than 100 electrons per nanorod. An increase in electron density was found to lead to an overall increase in scattering intensity and was described for the first time using Drude model derivations. The approach involved building large nanoparticle combinatorial libraries for high throughput screening.

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FA2386-14-1-4064

"High Throughput Spectroscopic Catalyst Screening by Surface Plasmon Spectroscopy"

Date July 15, 2015

PI and Co-PI information: Name of Principal Investigator – Paul Mulvaney; e-mail address –mulvaney@unimelb.edu.au; Institution - University of Melbourne; Department; Mailing Address – Bio21 Institute, Level 2 Nth, University of Melbourne,3 0 Flemington Road., Parkville, VIC., 3010, Australia; Phone = +61 8344-2405; Fax-+61-9348-1595.

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Abstract

We use dark field spectroscopy to monitor the dissociation of hydrogen on single gold nanoparticles embedded in metal oxide supports. Individual gold nanorods were monitored in real-time to reveal the peak position, the full width at half maximum and the relative intensity of the surface plasmon resonances during repeated N_2-H_2-N_2 and air-H_2-air cycles. Shifts in the spectra are shown to be due to changes in electron density and not to refractive index shifts in the environment. We demonstrate that hydrogen does not dissociate on gold nanorods (13 nm $\times$ 40 nm) at room temperature when in contact with silica and that electrons or hydrogen atoms migrate from Pt nanoparticles to Au nanoparticles through the supporting metal oxide at room temperature. However, this spillover mechanism only occurs for semiconducting oxides (anatase TiO_2 and ZnO) and does not occur for Au and Pt nanoparticles embedded in silica. Finally, we show that hydrogen does dissociate directly on anatase surfaces at room temperature during air-H_2-air cycles. Our results show that hydrogen spillover, surface dissociation of reactants and surface migration of chemical intermediates can be detected and monitored in real time at the single particle level.

To establish the ultimate sensitivity of the SPS technique, chemically synthesised gold nanorods (Au NRs approx 94 nm x 30 nm) were employed as individual optical elements in a quasi-solid-state ion-gel capacitor. We show that in such a device that the localised surface plasmon resonance (LSPR) of a single Au NR can be optically modulated rapidly by controlling the electron density on the nanorod periodically. The ion-gel device was highly transparent enabling the scattered light of individual Au NRs to be monitored using a supercontinuum-laser dark-field spectroscopy system. The laser system was developed to resolve the optical switching constant of individual Au NRs which was found to be less than 100 ms. Additionally at low voltages we detected smaller than 0.1% changes in scattering cross section at the flank of the half maximum which corresponded to the transfer of fewer than 100 electrons. We show that the increase in electron density leads to an overall increase in the scattering intensity and describe this for the first time using Drude model derivations.

Introduction:

Why the Work was done – Heterogeneous catalysis has taken on renewed importance as the push to find ways to obtain energy from renewable energy sources increases. Understanding reaction mechanisms is essential for the design of new catalysts that can improve the efficiency of water splitting, hydrogenation, CO oxidation and CO_2 reduction. We have carried out the first studies of the mechanisms of hydrogen adsorption on single particles using a new technique – surface plasmon spectroscopy. This idea is based on the fact that during redox reactions there will be small changes in electron density on a catalyst particle as reductants and oxidants exchange electrons with the particle. These cause minute changes in the scattered light of the particle. This technique is promising because by studying the kinetics of individual particles, we circumvent the problems of polydispersity in samples.

Key Outcomes and Accomplishments:

-We demonstrate " hydrogen spillover" on gold particle – metal oxide substrates. However, we do not find direct dissociation of hydrogen. Hydrogen does dissociate on Pt nanoparticles, and this is detected by adjacent gold nanoparticles.

-We demonstrate that equilibrium between hydrogen and gold takes several minutes to occur and that stored electrons are readily picked up by oxygen and protons.

-We show that spillover only occurs on semiconducting oxide supports like TiO2 and ZnO, but not SiO2. Electrons migrate 10-100nm through the matrix.

-We show hydrogen can also dissociate on TiO2 but only if it has been exposed to oxygen, which create acceptor sites on the oxide surface.

- We do not see direct dissociation of hydrogen on gold itself at room temperature.

A new flow-through, dark field spectroscopy system for studying CO oxidation has been set-up. However OH&S issues have slowed down experimentation. This has been rectified and the research will now focus on Pt/Pd as well as CO oxidation through a new PhD student.

Two methods for creating large scale nanoparticle libraries have been developed – capillary force assembly and electrophoretic deposition.

Advancing the Field:

Our work demonstrates that surface plasmon spectroscopy can monitor heterogeneous gas phase reactions on single particles and that the lower detection limit with " lock-in" techniques or signal averaging is less than 0.1% in the scattering signal. We have shown that the hydrogen interaction is strongly dependent on the matrix support used and the gas cycling process, for example whether N_2/H_2 cycles are used or air/H_2 cycles. Each cycle type prepares the

surface in a different state. Equilibrium is not as rapid as might be expected. Equilibration takes minutes in some cases but is quite reversible.

Introduction

(i) **Specific Aims** – Over the last decade, shape controlled synthesis of nanoparticles (NPs) has opened up the possibility to study heterogeneous catalysis on a variety of well-defined nanoscale crystal facets. The first step in heterogeneous gas catalysis usually involves the adsorption of a reactant onto a catalyst surface. A particularly important case is dissociative H_2 adsorption[1], which is well documented to occur on transition metal surfaces, producing mobile adsorbed H atoms[2]. These mobile surface H atoms play a central role in many catalytic processes such as hydrogenation reactions and understanding their chemical behavior is technologically important for high density hydrogen storage[3] and for the development of hydrogen sensing materials[4]. The discovery that mobile H atoms can migrate from the metal to the support matrix and then undergo further chemical reactions depending on the nature of the support and the presence of other sorbed species has been pivotal for catalysis. This cross-material migration process has been coined hydrogen spillover. **The goal of this work is to show that single particle surface plasmon spectroscopy (SPS) is a powerful tool for real-time monitoring of catalytic processes and chemical intermediates during surface redox reactions such as hydrogen spillover.**

(ii) **Importance** – The first evidence of hydrogen spillover was reported by Khoobiar in 1964 when it was observed that WO_3 underwent a colour change when it was reduced by H_2, but only in the presence of a Pt catalyst[5]. Since this discovery, H_2 molecule interactions with metal/oxide surfaces have been studied by a variety of techniques in order to understand spillover: product analysis[6], electrical conductivity[7], and infrared[8], nuclear magnetic resonance[9], electron paramagnetic resonance[10] and X-ray absorption spectroscopies[11]. Electrical conductivity measurements have been important in confirming that in Pt/TiO_2 materials, H atoms can migrate from the Pt to the reducible TiO_2 surface, remaining mobile in either the atomic (H∗) or ionic forms (H$^+$), with the possibility of both forms coexisting on TiO_2. Roland *et al.* showed that increases in conductivity occur in TiO_2 films that are in contact with, but at a suitable distance from, Pt catalysts exposed to H_2[12]. It was postulated that following chemisorption of hydrogen gas, there is an initial dissociation to form surface H atoms, some of which further dissociate into mobile electrons that transfer into the conduction band of the titania support, leaving protons bound to surface lattice oxide ions. However, a half century after its discovery, aspects of both spillover and reverse spillover remain contentious, despite thorough investigation *via* numerous experimental techniques. Recent review articles by Prins[13] and Roland *et al.*[14] discuss the challenges and uncertainties that persist in this area, many of which are due to the extreme difficulty of observing spillover directly.

Surface Plasmon Spectroscopy (SPS) – A New Technique – SPS has emerged a new tool to study the chemisorption of gases on metal nanocrystal surfaces[15, 16]. Au NPs exhibit strong extinction coefficients in the visible or NIR due to their ability to support a localized surface plasmon resonance (LSPR). The LSPR of Au NPs is sensitive to both dielectric constant changes in the supporting matrix and to changes in electron density on the metal. Both of these effects can be exploited to glean information about adsorption and desorption events. Initial reports used changes in the absorption spectrum of chemically synthesized Au NP ensembles to demonstrate detection and quantitation of reducing gases such as hydrogen and carbon monoxide [15, 17, 18]Optical shifts in Au NPs/metal oxide gas sensors are often considered to be the consequence of electron exchange on the metal at the metal/oxide interface, as well as an effect of dielectric changes in the support[19, 20]. It is therefore crucial to understand the separate contributions that modifying the free-electron density on the plasmonic particles and the dielectric function of the supporting medium have on LSPR changes. Buso *et al.* and Della Gaspera *et al.* concluded that LSPR changes from H_2 reduction of Au/TiO$_2$ and Au/TiO$_2$/Pt films is induced by the production of free electrons and subsequent charge transfer to the Au NPs[15, 21]. This conclusion was supported by the work of Carpenter *et al.*, where it was found that this mechanism was the main driver of LSPR shifts on Au/yttrium-stabilized-zirconia films when exposed to H_2[22]. In contrast to LSPR charge transfer driven shifts, Larsson *et al.* attributed changes in the gold particle spectra to H_2 induced dielectric function changes of nearby Pt NPs separated by a SiO$_2$ support[23].

More recent studies showed that gas sorption can be followed even at the single particle level by dark-field microscopy (DFM). DFM was first used to measure the interaction of hydrogen with single metal NPs by Liu *et al.,* who used lithographically fabricated systems of single Pd NPs close to the tip of a Au nanoantenna to monitor dielectric changes of the Pd component during hydrogen exposure[24]. Following this, Tang *et al.* revealed the shape dependence of the hydrogen uptake process studying changes to the dielectric function of a Pd shell on Au cores[25] and Tittl *et al.* used silica shell-isolated Au NPs to investigate the dielectric changes during hydration of a Pd film[26]. However, the fundamental challenge for catalysis is to investigate the more complex problem of the metal catalyst-support interaction.

By measuring electron transfer at the single particle level we show in this study that the H_2 adsorption mechanism on Au and Pt NPs strongly depends on the metal oxide support (TiO$_2$, ZnO and SiO$_2$). This highly sensitive technique is enabled by the use of low-scattering, thin films prepared by sol-gel synthesis. While DFM has been used previously to directly measure electron transfer[27, 28], this is the first case where charge transfer processes with gas phase reactants on single metal NPs

have been measured directly. SPS measurements on single particles have larger signal-to-noise ratios than ensemble measurements when there is a low level of Au NP loading. A low metal loading removes Au NP-Au NP optical coupling which simplifies the SPS analysis. Furthermore, it enables proximity effects between Au and Pt NPs to be determined in a straight-forward manner because a submonolayer of Au NPs on a flat plane has a more uniform, three dimensional environment than a multilayer or a mixed layer. **We use the single particle spectroscopic information to unambiguously show that hydrogen is mobile and undergoes spillover from Pt to Au NPs.**

(iii) Ultimate Goal - Our ultimate goal is to extend these systems to different heterogeneous reactions and to determine which crystal facets determine the overall catalytic efficiency of different nanoparticles. We also aim to build alrge combinatorial libraries of nanoparticles for high throughput screening.

Experiment:
Characterization
Ensemble absorbance spectra were collected with an Agilent 8453 UV-visible spectrophotometer, between 200-1000 nm. Optical constants n and k and film thicknesses were evaluated by measuring the variables Ψ and Δ with a J. A. Wollam V-VASE Spectroscopic Ellipsometer at two angles of incidence (60° and 70°) in the wavelength range of 300-1500 nm. Optical constants n and k and film thickness were evaluated from Ψ, Δ data using the WVASE32 ellipsometry data analysis software. The data were fitted with Cauchy dispersion and Tauc-Lorentz oscillators in the non-absorbing region and at the UV absorption edge, respectively. Transmission electron microscopy (TEM) images were acquired on a FEI Tecnai TF20 microscope operating at 200 kV. TEM samples were prepared by drop casting the sample solutions onto copper TEM grids (300 carbon mesh) and drying in ambient conditions. Scanning electron microscopy (SEM) was performed on a FEI Nova 200 Nanolab microscope operating at 5 kV.

Characterization of the Au NRs is reported in Figure S1, from which it is possible to note that the Au NRs had an aspect ratio of 3 with a longitudinal LSPR centered at 810 nm. The refractive indices of the layers used for covering the Au NRs were 1.43, 1.95 and 1.72 for SiO_2, TiO_2 and ZnO respectively (at 630 nm). The metal oxide layer thicknesses were 100, 30 and 30 nm for the SiO_2, TiO_2 and ZnO films respectively. From the SEM images in Figure S2, it is evident that the films were homogeneous and smooth.

Single particle spectroscopy measurements
Single-particle time-resolved measurements were carried out using a Nikon TE2000-S Eclipse inverted microscope equipped with a Nikon dry dark-field

condenser and a 40X/0.6 NA ELWD dry objective lens in transmission configuration. A Princeton Instruments Isoplane SCT 320 imaging spectrograph fitted with a PIXIS 1024F CCD detector was coupled to the image output of the microscope for spectroscopic measurements (Figure 3). The samples were placed in a custom made cell in which the scattering spectra could be collected in transmission under different atmospheres. The measurements were taken at room temperature (RT) using 50,000 ppm H_2, balanced with N_2 (5% H_2 in N_2), with a flow rate of 5 L/hr. The gases used in these experiments were all high purity grade (< 10 vpm C_nH_m) with very low water content (< 15 vpm). All N_2-H_2-N_2 and air-H_2-air cycles were 60 minute-30 minute-60 minute in duration. Using the DFM, Au NR spectra were captured every 60 seconds during 4 cycles of exposure to 5% H_2 in N_2, with N_2 or air as the alternating gas. The imaging spectroscopy system had the ability to measure the scattering spectra of multiple, well-distributed AuNRs simultaneously enabling the surface plasmon band position of 3-10 particles to be tracked at the same time. This provided greater statistical certainty about the spectral response of a typical single particle during each experiment within the same sample, and a typical single particle kinetic trace could therefore be selected to be representative of the sample as a whole. An automated image-to-spectrum extraction and Lorentzian fitting procedure was carried out on the data using IGOR Pro software to execute fast and accurate analysis of hundreds of image files collected during each experiment. Prior to running the procedure, the pixel rows of a Au NR-free area of the image in close proximity to the Au NRs being analyzed was subtracted from the signal to remove the background contribution from the substrate and oxide layer. Examples of the scattering intensity of the background varying with time have been included in the supporting information (Figure S7) to illustrate the stability of these signals during the gas cycles. The baseline of the single particle spectra of an oxide supported Au NR did not always reach zero. This is due to the slight inhomogeneity of background scattering that was caused by the oxide matrix and the Pt NPs, and could lead to a less effective background correction. If the background signal that was selected for the procedure had a different level of scattering intensity than the small area the Au NR is situated in, the background correction might not have been completely effective in removing the scattering contribution of the surrounding matrix from the Au NR signal. Nevertheless, regular, quasi-Lorentzian lineshapes at intensities expected for single Au NRs of these dimensions were measurable and Lorentzian fitting could be effectively applied to the data extracted. Hence, while automation resulted in enormous efficiency gains, there was a small but noteworthy drawback in accuracy.

The experiments typically ran for six hours, which resulted in slow long-term drifts in the focal position of the microscope. Over this time the focal position could influence the absolute value of LSPR peak position due to chromatic aberrations present in the objective lenses. An additional focal drift correction was

made by fitting a trend line to the data and normalizing the data to the fit function, where the long-term changes in the data were clearly not due to the introduction of different atmospheres into the gas chamber.
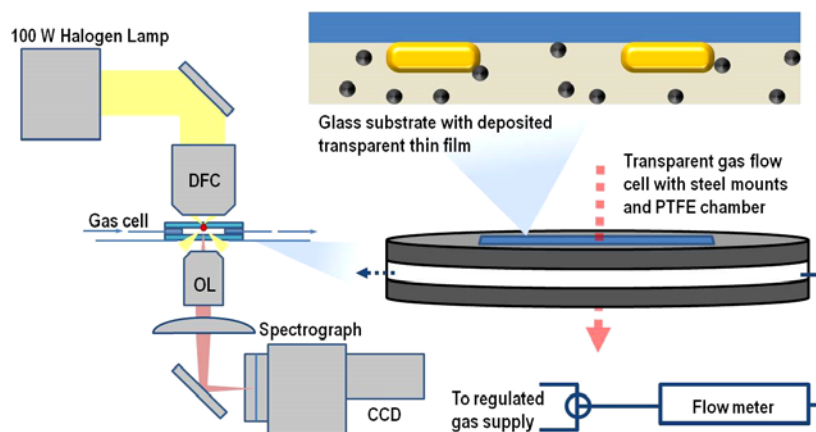

Figure 1. Optical setup for single particle gas measurements. An optical inverted microscope fitted with a dry dark-field condenser (DFC) and 40x objective lens (OL) is coupled to an imaging spectrometer with an array detector (CCD). To the right, a larger view of the home built transmission gas cell with a micro-schematic view of an example thin-film on the underside of the top window.

Results and Discussion:
Key Experiments and Findings. For a fuller account please see Publication 1 below.

A. Surface Plasmon Spectroscopy of Hydrogen Adsorption

Sample	Sample name	Composition	Schematic
A	Au	Bare AuNRs on glass	
B	Au/Pt	Au NRs and Pt NPs on glass	
C	Au/TiO$_2$	AuNRs on glass covered with a TiO$_2$ film	
D	Au/TiO$_2$-Pt	Au NRs on glass covered with a TiO$_2$ film containing 8 wt% Pt NPs	
E	Au/ TiO$_2$/Pt	Au NRs on glass covered with a TiO$_2$ film with Pt NPs deposited on top	
F	Au/ SiO$_2$-Pt	Au NRs on glass covered with a SiO$_2$ film containing 8 wt% Pt NPs	
G	Au/ZnO	Au NRs on glass covered with a ZnO film	
H	Au/ZnO-Pt	Au NRs on glass covered with a ZnO film containing 8 wt% Pt NPs	

Figure 2: List of samples studied. We used three different spin coated films of TiO2, ZnO and SiO2. Wwe used gold nanorods and Platinum nanocrystals as model catalysts and we used air-H2 or N2-H2 cycles to study adsorption and esporption dynamics. All experiments were done at room temperature.

A crucial finding of this project was the need to do careful blanks. Nanoparticles are " connected" by electronic and ionic pathways, as well as by and molecular diffusion, to the substrates.
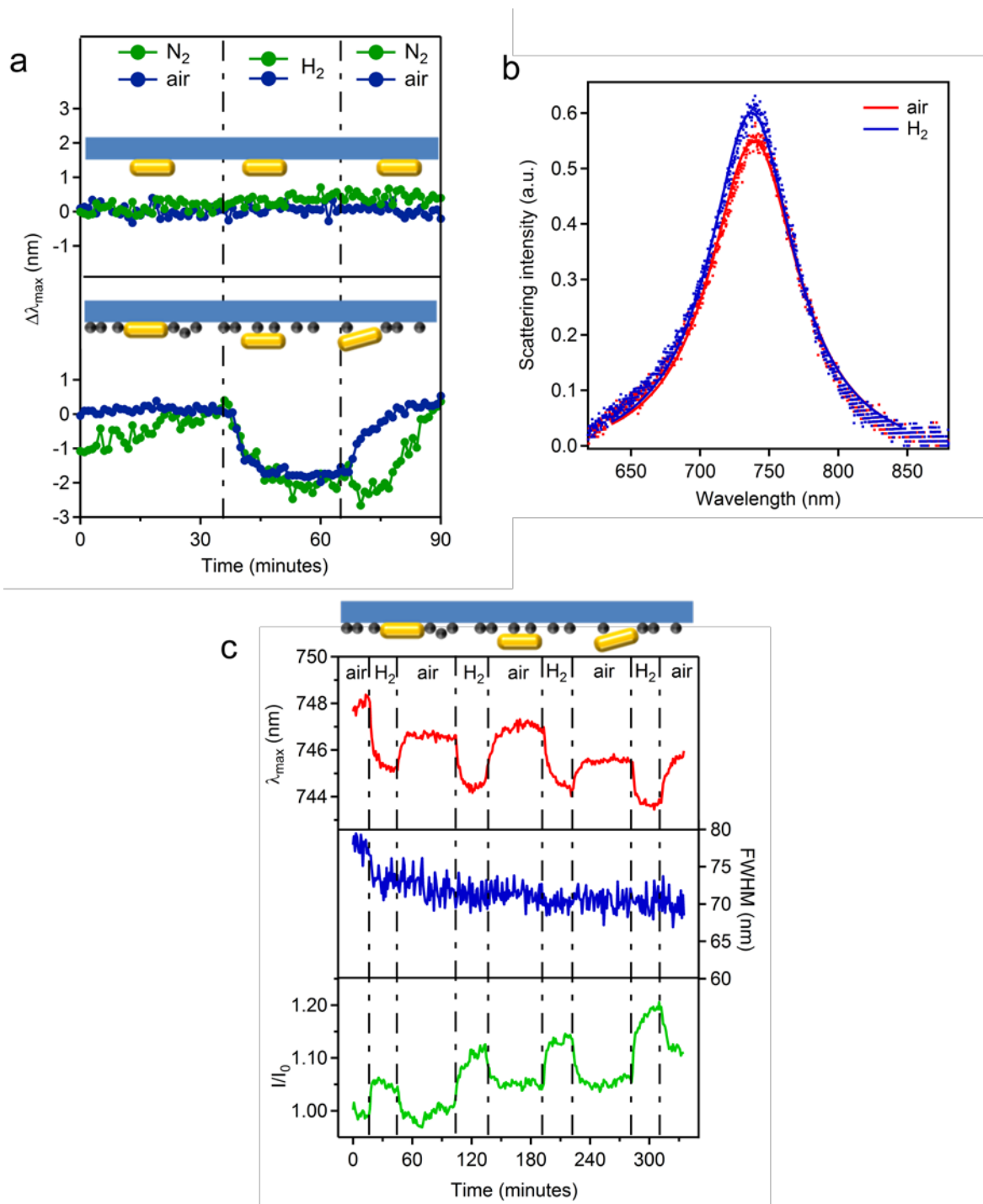
Figure 3. Gas interaction results for a typical single particle on glass in the Au and Au/Pt samples. (a) A comparison of $\Delta\lambda_{max}$ for a single Au NR in the Au sample (top figure) and a single Au NR in the Au/Pt sample in the fourth $N_2-H_2-N_2$ (green) and air$-H_2-$air (blue) cycle. (b) A comparison of scattering spectra for a single Au NR in the Au/Pt sample on the fourth air$-H_2-$air cycle in air (red) and H_2 (blue) after 30 minutes. (c) A full temporal and spectral analysis of λ_{max} (red), FWHM (blue), and I/I_0 (green), of a single Au NR in the Au/Pt sample during repeated cycles of air$-H_2-$air at RT.

They interact with the substrate. Chemical intermediates can transfer from particle to particle as we show below. In our SPS studies we used 8 different types of sample. Our initial experiment was actually sample C using air/H2 cycles. We saw SPS shifts and deduced that hydrogen dissociated on gold nanorods at room temperature. This turns out to be wrong!

From Figure 3a, we see that the spectrum of the rod does not change on glass. There is no dissociation of hydrogen gas on the nanorod. If Pt nanocrystals are present we do see shifts. Remember that we are looking at the gold spectrum only. We do not see the Pt particle. From this we deduce that dissociation of hydrogen occurs on Pt but this leads to electron density increases (blue-shift) in the gold spectrum.

Figure 4 shows some useful other experiments. Firstly much bigger shifts are found when the rods are coated with TiO_2. There is much more dissociation, the dynamics are much, much faster and very reversible (seconds instead of tens of minutes). Figure 3d and e are most interesting. Figure 3d shows that when the Pt nanoparticles are 30nm away from the gold, the gold still blue-shifts. Hence dissociation of H_2 on the Pt leads to a flow of either H atoms or electrons through the TiO_2 to the gold. However Figure 3e shows that if the same experiment is done with a silica matrix, no charging of gold occurs. Hence the electrons or H atoms do not migrate across the silica substrate.

These key findings show that SPS can provide direct evidence about the mechanisms of gas catalysis on nanoparticle surfaces.
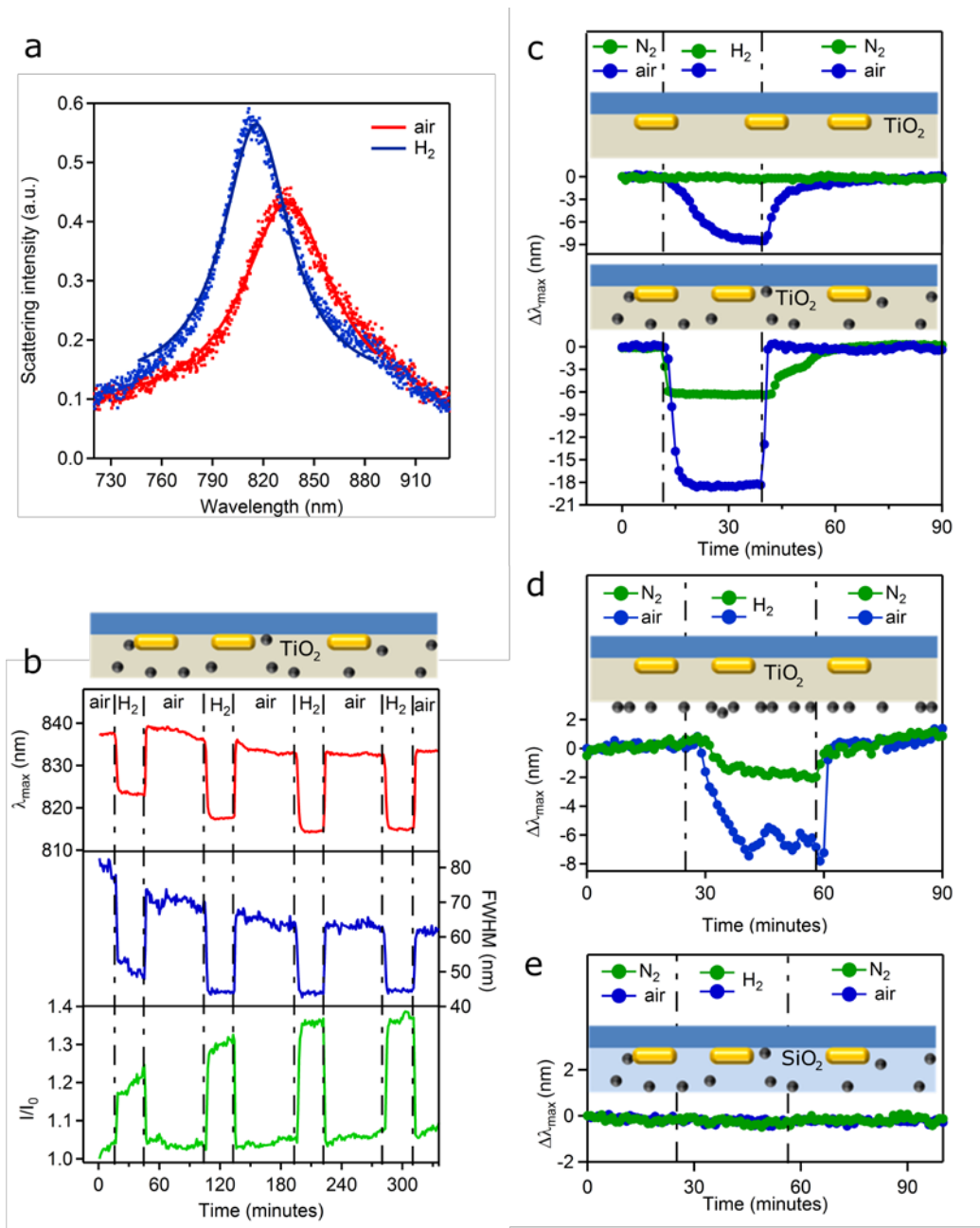
Figure 4. Gas interaction results for a typical single particle in the 30 nm thick Au/TiO$_2$, 30 nm thick Au/TiO$_2$–Pt, 30 nm thick Au/TiO$_2$/Pt and 100 nm thick Au/SiO$_2$–Pt samples. (a) A comparison of scattering spectra for a single Au NR in the Au/TiO$_2$–Pt sample on the fourth air–H$_2$–air cycle in air (red) and H$_2$ (blue) after 30 minutes. (b) A comparison of $\Delta \lambda_{max}$ for a single Au NR in the Au/TiO$_2$ sample (top) and a single Au NR in the Au/TiO$_2$–Pt sample (bottom) in the fourth N$_2$–H$_2$–N$_2$ (green) and air–H$_2$–air (blue) cycle. (c) A full temporal and spectral analysis of λ_{max} (red), FWHM (blue), and I/I$_0$ (green), of a single Au NR in the Au/TiO$_2$–Pt sample during repeated cycles of air–H$_2$–air at RT. A comparison of $\Delta \lambda_{max}$ for a single Au NR in the Au/TiO$_2$/Pt sample (d) and in the Au/SiO$_2$–Pt sample (e) in the fourth N$_2$–H$_2$–N$_2$ (green) and air–H$_2$–air (blue) cycle.

B. Improving the Sensitivity. What is the smallest number of electrons we can see on a particle?

To establish the ultimate limis of senstivity of the system and improve the dynamic range down to sub-second timscales, we have constructed a pulsed white light source for monitoring the reactions more quickly and detecting much smaller spectral shifts as shown in Figure 5 (left). Spectra can be collected point by point (right). The modified system is shown below.
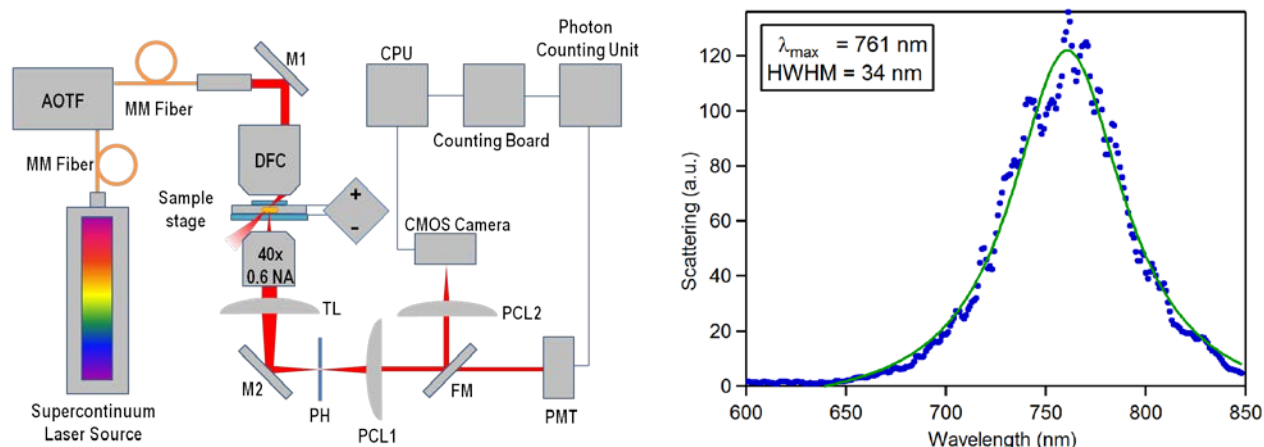

Figure 5. (a) Schematic diagram of the laser spectroscopy set up. AOTF = acousto-optical tunable filter, MM = multimode, M = mirror, DFC = dry dark field condenser (0.8-0.95 NA), TL = tube lens, PH = 100 μm pin hole, PCL = planoconvex lens, FM = flip mirror, PMT = photon multiplier tube, CMOS = complimentary metal-oxide semiconductor, CPU = computer. (b) AOTF scan generated scattering spectra of a single AuNR under no external voltage.

To put charge onto single nanoparticles, we fabricated an ITO parallel plate capacitor using patterned ITO. An ionogel was used as spacer. (Figure 6).
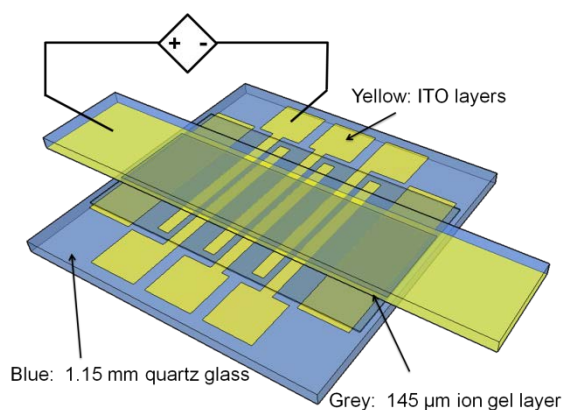

Figure 6. (a) Schematic representation of the transparent ion gel capacitor device structure. Two pieces of quartz glass with 140 nm layers of ITO are sandwiched together with a 145 μm thick ion gel layer in between. The 25 mm × 25 mm bottom piece of ITO was photolithographically patterned to create six separate

cathodes with a 2 mm × 10 mm active area. The whole patterned substrate was then functionalised with a monolayer of (3-mercaptopropyl)trimethoxysilane and then a 40 pM colloidal solution (200 μ L) of chemically synthesised 30 nm × 94 nm gold nanorods was spun cast on top at 2000 rpm (1000 acceleration) for 120 seconds. Following this, 200 μ L of freshly prepared ion gel solution was spun cast on top at 3000 rpm (500 acceleration) for 60 seconds. On the top electrode, a 10 mm × 35 mm piece of unpatterned ITO, 100 μ L the same ion gel solution was distributed evenly over the surface by drop casting. Both device substrates were then dried in a vacuum oven at 60 °C for 18 hours to remove residual solvent.
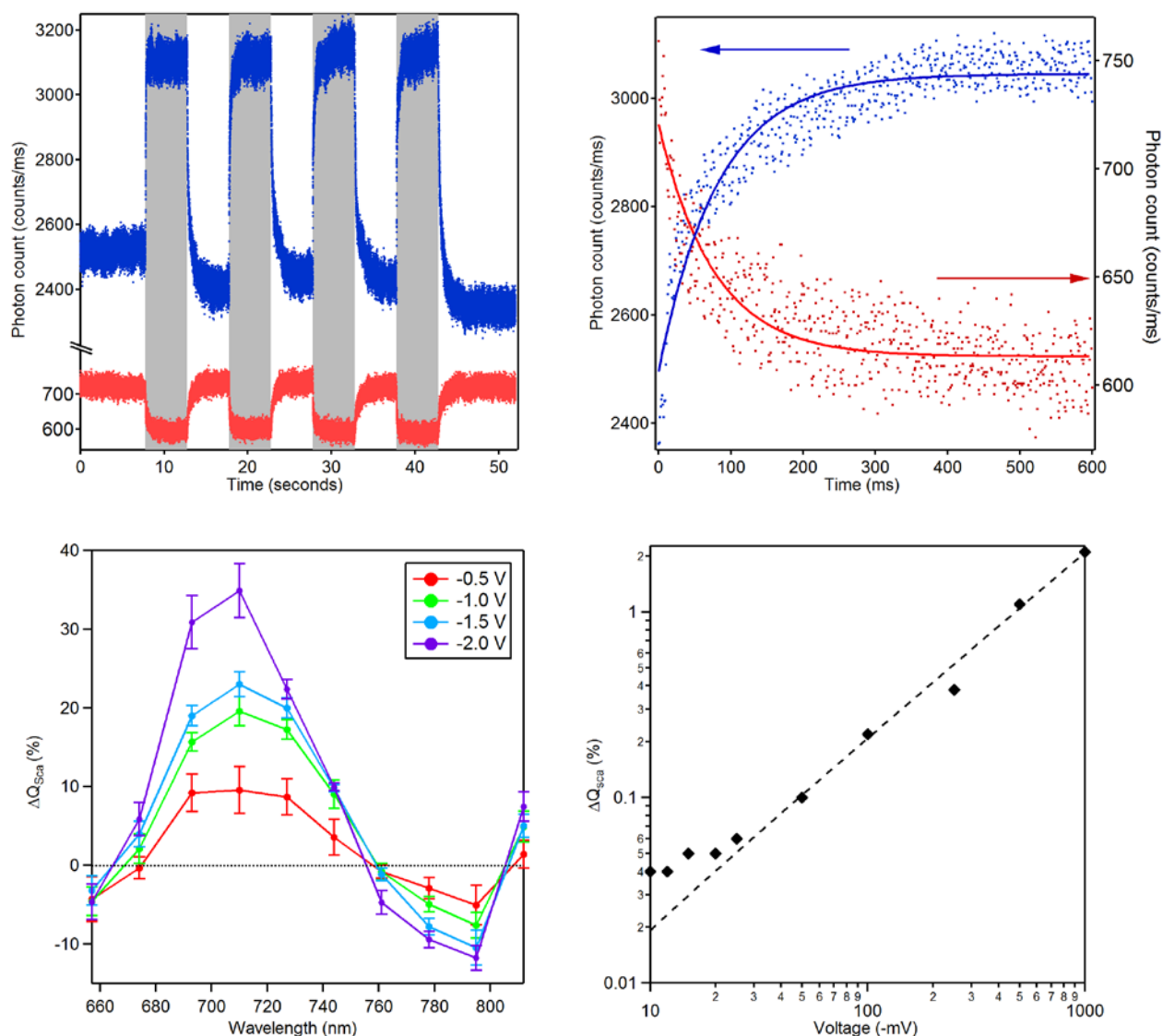

Figure 7. Time-resolved kinetic charging data acquired using the laser spectroscopy set up. (top left) Photon count per millisecond against time of the blue flank at half maximum (blue trace) and red flank at half maximum (red trace), during 4 cycles of 0 V (white background) to -2 V (grey background). (top right) Optical response of charging (dots) with single exponential fits (lines) for the blue and red flanks. Lower figures: Change in scattering cross section (bottom left) for

set wavelengths over the longitudinal band at different applied voltages from a potentiostat and (bottom right) for different applied potential from a wave function generator using the average ΔQ_{sca} over 200 square wave cycles at 0.5 Hz to enable much lower values to be measured.

The Fianium laser allows us to follow changes in scattering at one wavelength with a high intensity light signal to pick up small changes in signal. For this we use a PMT rather than the spectrograph, which is slower. By using the electrochemical cell filled with a conducting iongel to make it a "solid state" device, we can apply controlled amounts of charge to the particles and calibrate the system. The smallest detectable changes occurred fro 10mV applied voltages, which yielded less than 100 electrons per nanorod.

C. Nanoparticle Arrays

Student Tim Mapperson has been completing this aspect and it will be covered in his PhD thesis to be submitted in 2015. Although we can create arrays 100 particle x 100 particles arrays routinely (see trimer arryas below left), larger micron to millimetre scale arrays have been harder. Figure 8 shows bright field image of arrays of gold rods in 30 micron squares. We see that the arrays are densely and poorly packed with particles.
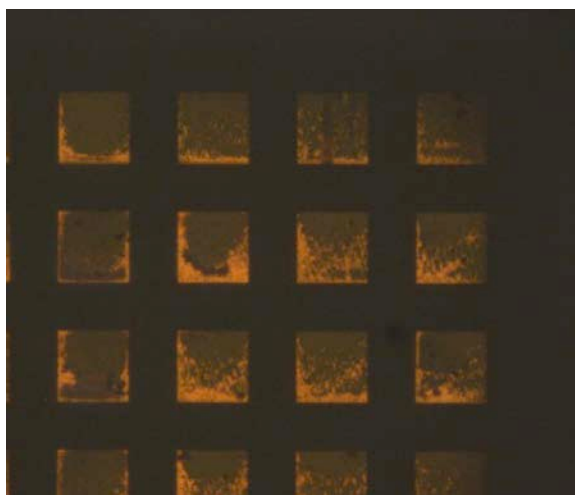

Figure 8: Typical dark field microscopy image of gold nanoparticle arrays showing very inhomogeneous filling. 30 micron squares.

In the dark field flow system, we pass colloidal solutions over an area of several square centimetres. The goal is to fill each EBL fabricated hole with a single nanoparticle. There are several tens of millions of holes per square centimetre.
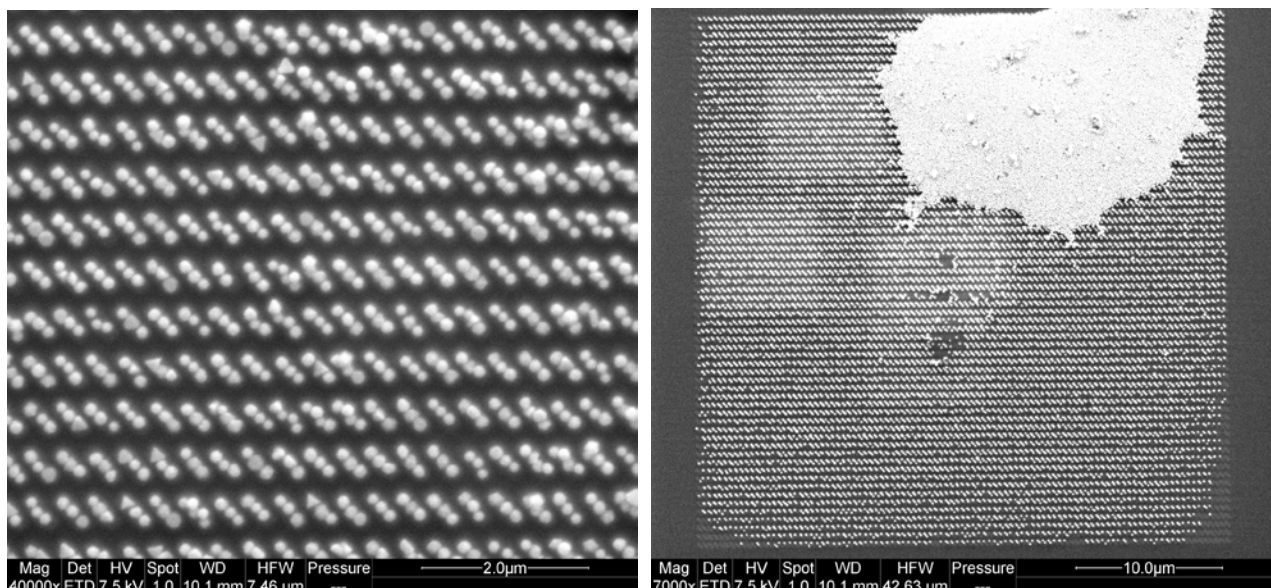
Figure 9: (left) Typical electron microscopy images of gold nanoparticle arrays. The squares are around 30 microns across and have been patterned with dense arrays of oblong holes around 200nm long and 80nm wide using PMMA. On the left, high ordering of gold spheres 50nm in diameter into trimers in each hole. Scale bar 2microns. (Right) a typical square at larger length scale – scale bar 10 microns.

In Figure 9 (right) we see an extremely ordered array of gold nanoaparticles, However it is marred by EBL template flaws in the middle and a large dried out gold particle film at the top. These lithographic imperfections and difficulties in controlling the pinning of the capillaries has made it difficult to create " catalyst libraries" . As a result we will shift to using electrophoretic deposition or chemical assembly methods in late 2015 (Heyou Zhang, PhD).

In summary, while the concept of the catalyst library is a powerful one there are still key hurdles to overcome.

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List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

Outputs
a) Publications
1. " Hydrogen Spillover between Single Gold Nanorods and Metal Oxide Supports – A Surface Plasmon Spectroscopy Study" , Sean S. E. Collins, Michela Cittadini, Carlos Pecharromán, Alessandro Martucci, and Paul Mulvaney, ACS Nano (accepted July, 2015). See attachment.

2. " Spectroelectrochemistry of Silver Deposition on Single Gold Nanocrystals" , Mariana Chirea, Sean S. E. Collins, Xingzhan Wei and Paul Mulvaney, *J. Phys. Chem. Lett.* 5, 4331－4335 (2014). See attachment.

b) Conference Proceedings – N/A.
c) **Conferences and Presentations**

1. Sean Collins presented this at the ACS Denver March 2015 and MRS San Francisco April 2015.
2. Paul Mulvaney presented the key findings at a seminar at Notre Dame Chemistry Department in March 2015.
3. Sean Collins presented this work at Rice University in April 2015.

d) " Single gold nanocrystal optical switching" , *Sean S. E. Collins, Xingzhan Wei, Thomas G. McKenzie, Alison Funston, Paul Mulvaney* Nano Letters (submitted)

e) Interactions with USAF Staff
There have been no interactions to date except through the program manager.

DD882: As a separate document, please complete and sign the inventions disclosure form.